



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

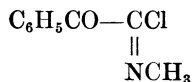
a glass rod, it becomes solid. The substance is recrystallized from a mixture of ether and ligroine (bpt. 40° to 60°), using animal charcoal, and obtained in pale yellow heavy many-sided crystals, melting at 74°. It is little soluble in cold, but readily soluble in hot water, and comes out on cooling in prisms. In organic solvents, except ligroine, it is easily soluble.

0.1970 gram dried over H_2SO_4 in a vacuum gave 0.4775 gram CO_2 and 0.1044 gram H_2O .

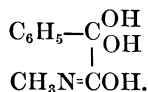
0.2034 gram gave 15.5 c.cm. N_2 at 4° and 735 mm.

	Theory for $\text{C}_6\text{H}_5\text{NO}_2$.	Found
C	66.25	66.11
H	5.52	5.88
N	8.59	9.05

Benzoylformic-methylamide has thus been obtained from the addition product

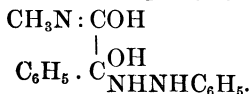


first formed. The substance is easily soluble in cold dilute sodic hydrate, but on addition of dilute sulphuric acid it is not precipitated again. Ether extracts an oily substance soluble in water, which slowly, on standing over sulphuric acid in a vacuum, gets solid. The solid product is insoluble in water, and crystallizes from acetic ether in needles melting at 143°; this is probably a polymer, whereas the oily substance is a hydrate,



The substance shows thus in its behavior great resemblance to benzoylformic-amide, which Claisen has shown* exists in two modifications (probably polymeric), and also forms a low melting hydrate.†

Benzoylformic-methylamide-phenylhydrazonhydrate,



On treating benzoylformic-methylamide in concentrated ethereal solution at 0° with an ethereal solution of phenylhydrazine (one molecule),

* Ber. d. chem. Ges., XII. 633.

† Ann. Chem. (Liebig), CCLXX. 295, 300, 316.

a white voluminous precipitate separates out in flakes, which, after being well washed with ether, dried on a clay plate and a short time over sulphuric acid in a vacuum, was directly analyzed.

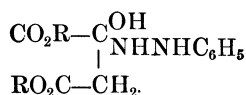
0.2056 gram substance gave 0.5037 gram CO_2 and 0.1202 gram H_2O .

0.1551 gram substance gave 20.5 c.cm. N_2 at 6° and 745 mm.

	Theory for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_2$	Found.
C	66.42	66.77
H	6.27	6.49
N	15.50	15.78

Phenylhydrazine has thus simply added itself to the carbonyl group present in benzoylformicmethylamide, giving rise to a hydrazonehydrate. It is insoluble in water, and is not split into its components by cold sodic hydrate, but possesses a great tendency to lose water, becoming thereby yellow and sticky.

In this connection I would like again to point out that the product which W. Wislicenus* has obtained from oxalacetic ether and phenylhydrazine cannot possibly be a hydrazonehydrate,



because it possesses entirely different properties from the hydrazonehydrates obtained by myself,† which under no condition can be split into their components by means of alkalies. The substance obtained by W. Wislicenus shows a totally different behavior; it is, just as phenylhydrazine hydrochloride, a salt-like compound, and is therefore split immediately by alkalies into its components.

Benzoylformic-phenylhydrazone from benzoylformic-methylamide.

That the compounds just described are derivatives of phenylglyoxylic acid is very probable. The poeof of this is furnished as follows: 3 grams benzoylformic-methylamide-phenylhydrazonehydrate are warmed on a water bath for half an hour with 80 c.cm. dilute ten per cent sodic hydrate (the hydrazonehydrate dissolves readily on gentle warming). A strong smell of methylamine is noticed, and on adding dilute hydrochloric acid a yellow flaky precipitate (1.4 grams) comes down, which is dissolved again in soda and reprecipitated by acids. The method of

* Ber. d. chem. Ges., XXIV. 3007

† Ann. Chem. (Liebig), CCLXX. 292, 300, 319, 333.

purification used by Elbers * does not yield an absolutely pure product; it is much better to recrystallize from benzene, wherein the substance is readily soluble on heating, but practically insoluble in the cold. Yellow needles melting at 163° (Elbers gives mpt. 153°) were thus obtained.

0.1661 gram substance, dried at 90° , gave 0.4259 gram CO_2 and 0.0750 gram H_2O .

0.1008 gram substance, dried at 90° , gave 11 c.cm. N_2 at 25° and 739 mm.

	Theory for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$.	Found.
C	70.00	69.93
H	5.00	5.02
N	11.66	11.82

Molecular Rearrangement of Ethylisocyanide to Propionitrile.

Ethylisocyanide was made according to the method of Gautier,† by heating 100 grams silvercyanide and 115 grams ethyliodide for one and one half hours on a water bath (with reversed condenser and with a mercury valve). The substance (bpt. 79°) can be kept for fifteen months without the slightest change. It can be heated without any essential change for many hours to 210° ; a slight yellow coloration only is noticed.‡ The first statements of Gautier§ concerning this substance, which he does not mention in his later paper,|| are therefore to be corrected. On heating ethylisocyanide, however, to a still higher temperature, molecular rearrangement to ethylcyanide takes place almost quantitatively. 7.5 c.cm. ethylisocyanide are heated in a sealed tube for three hours between 230° – 255° , and the contents of the tube, which are colored brown and smell slightly of ammonia and isocyanide, distilled off. Everything came over except a slight residue between 94° and 98° . In order to remove ammonia and traces of isonitrile, the oil was washed with a chloride of calcium solution containing hydrochloric acid, and then dried with solid calcic chloride. On distilling, a pleasant ethereal smelling oil, boiling constant at 97° , was obtained (4 c.cm.), which was identical in every respect with propionitrile.

0.1528 gram substance gave 0.3668 gram CO_2 and 0.1278 gram H_2O .

0.1530 gram substance gave 33.5 c.cm. N_2 at 9° and 741 mm.

* Ann. Chem. (Liebig), CCXXVII. 341.

† Loc. cit., [4.], XVII. 233.

‡ Comptes Rendus, LXV. 862.

§ Loc. cit., [4.], XVII. 236.

|| Ibid., 203–260.

	Theory for C_3H_5N .	Found.
C	65.45	65.46
H	9.09	9.29
N	25.45	25.66

The Action of Sulphur on Ethylisocyanide.

7.5 c.cm. ethylisocyanide, 3.1 grams crystallized sulphur, and 15 c.cm. carbonbisulphide were heated in a sealed tube at 110° – 120° for two hours. The reaction is complete, and the mustard oil formed is driven over with steam, extracted with ether, and, after drying with calcic chloride, is fractionated. It boils constant at 131° , and is identical with ethyl-mustard oil first isolated by Hofmann.*

0.2040 gram burnt with lead chromate gave 0.3063 gram CO_2 and 0.1016 gram H_2O .

0.2544 gram substance gave 0.6771 gram $BaSO_4$ (Carius).

	Theory for C_3H_5NCS .	Found.
C	41.88	40.95
H	5.75	5.50
S	36.78	36.55

The Action of Hydrogen Sulphide on Ethylisocyanide.

Thioformethylamide, $C_2H_5N : C \begin{smallmatrix} H \\ SH \end{smallmatrix}$. 10 c.cm. ethylisocyanide were dissolved in 200 c.cm. absolute alcohol, saturated at 0° with hydrogen sulphide, and then heated for 4 hours in a sealed tube at 100° . The isonitrile smell was entirely gone, and, after distilling off the alcohol, the brown oily residue was fractionated under reduced pressure. The chief portion boiled at 140° – 150° at 40 mm. pressure, and, on the second distillation, a yellow oil, smelling of sulphur, and boiling at 125° at 14 mm. pressure was obtained.

0.1996 gram substance, burnt with lead chromate, gave 0.2980 gram CO_2 and 0.1468 gram H_2O .

0.2034 gram substance, gave 29.5 c.cm. N_2 at 18° and 737 mm.

0.2885 gram substance gave 0.7529 gram $BaSO_4$ (Carius).

	Theory for C_3H_7NS .	Found.
C	40.45	40.71
H	7.87	8.17
N	15.73	16.23
S	35.95	35.84

* Ber. d. chem. Ges., I. 26.

Ethylisocyanchloride or Ethylimidocarbonylchloride, C₂H₅N=CCl₂.

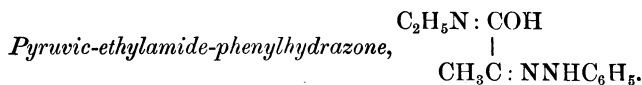
On passing dry chlorine over a solution of 10 c.cm. ethylisocyanide in 40 c.cm. chloroform, the gas is absorbed instantly, without the slightest trace of hydrochloric acid or of coloration being noticeable. As soon as the solution is colored yellow, or smells of chlorine, it is directly fractionated. It was possible to obtain a small amount of a colorless, very sharp-smelling oil, boiling at 99°–100°. Since, however, the separation from the large amount of chloroform can only be accomplished with much loss of material, the ethylisocyanchloride is better prepared as follows: 5 c.cm. ethylisocyanide, diluted with four times its volume of absolute ether, are cooled to –15° and 5.5 c.cm. sulphurylchloride are slowly added. An energetic reaction takes place, and the solution becomes colored yellow and smells strongly of sulphurdioxide. After ten minutes' standing, the solution is washed with dilute sodic hydrate, and then dried with calcic chloride. On fractionating, a colorless, intensely sharp-smelling oil, boiling at 102°, is obtained.

0.2994 gram substance gave 0.3183 gram CO₂ and 0.1101 gram H₂O.

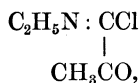
0.2450 gram substance gave 0.5536 gram AgCl (Carius).

0.1575 gram substance gave 14.5 c.cm. N₂ at 8° and 745 mm.

	Theory for C ₃ H ₅ NCl ₂ .	Found.
C	28.57	28.99
H	3.97	4.09
N	11.11	10.90
Cl	56.35	55.90

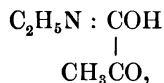
The Action of Acetylchloride on Ethylisocyanide.

Ethylisocyanide (7.5 c.cm.) and acetylchloride (6.5 c.cm., one molecule) react on each other when mixed together readily at 0°, and the solution becomes colored yellow. After standing for twelve hours at ordinary temperature, a dark brown liquid is obtained, which was divided into two portions, *a* and *b*. On fractionating *a*, it all distilled over between 50° and 60° at 15 mm. pressure, as a yellow oil which, redistilled at ordinary pressure, boils at 100°–130°. In both cases the oil smells of isonitrile, so that a dissociation of the ethylimidopyruvylchloride,



into its components must take place on distillation, and an analysis of the substance would therefore be of no value. One encounters here, as has also been observed in the case of many other addition products of the isocyanides,* the remarkable property that these are easily split into their components, either at higher temperatures, or on standing in the cold, or on treatment with sodic hydrate; whereas, on the other hand, these components either at -20° or at ordinary or higher temperatures often unite with explosive violence. *Bivalent carbon therefore behaves exactly like trivalent nitrogen* in ammonia and the amines, since also the last named compounds unite often with explosive violence with acids, e. g. hydrochloric acid, forming addition products containing quinquivalent nitrogen, which in turn, either by heating or by treating with alkalis, are split into their components.

That the above distilled oil *a*, however, still contains much ethylimidopyruvylchloride, is shown by decomposing it with water: it is converted thereby into pyruvic-ethylamide,



the presence of which in the aqueous solution, since it cannot be extracted therefrom by ether, is best shown by adding phenylhydrazinehydrochloride, which precipitates an insoluble hydrazone (3.5 grams).

The above mentioned portion *b* was not distilled, but decomposed directly with ice water, and the reddish-colored solution treated with phenylhydrazinehydrochloride, and thus 7.7 grams insoluble hydrazone were obtained. The hydrazone is obtained, when recrystallized from alcohol, in colorless many-sided heavy crystals, melting at 165° . It is insoluble in alkalis and in water.

0.2002 gram substance, dried at 100° , gave 0.4731 gram CO_2 and 0.1387 gram H_2O .

0.1494 gram substance, dried at 100° , gave 27.5 c.cm. N_2 at 20° and 747 mm.

	Theory for $\text{C}_{11}\text{H}_{16}\text{N}_3\text{O}$.	Found.
C	64.39	64.44
H	7.31	7.69
N	20.49	20.69

* Ann. Chem. (Liebig), CCLXX. 297, 298, 322.

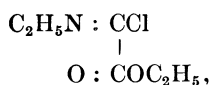
The Action of Phosgene on Ethylisocyanide.

On adding slowly 5 c.cm. phosgene (cooled to -15°) to 10 c.cm. ethylisocyanide (cooled to -19°), reaction takes place always with explosive violence. Even when the isocyanide is diluted with an equal volume of absolute ether and the solution is cooled to -19° , a very energetic union takes place on adding the phosgene, which makes it difficult to regulate the reaction. A yellow sharp-smelling liquid is formed, which does not boil without decomposition. On pouring it into water a brown solution containing much hydrochloric acid is formed, from which ether extracts nothing, and which gives no precipitate with phenylhydrazine. The products, which are in all probability all derivatives of mesoxalic acid,* were not further investigated.

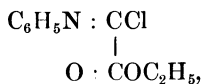
The Action of Chlorocarbonic Ether on Ethylisocyanide.

An addition of chlorocarbonic ether, or of alkyl iodides or chlorides, to aromatic derivatives of isocyanogen could not be accomplished, because a reaction takes place only at high temperatures, and this must result in the formation of much resinous polymeric products, as well as in the decomposition of the addition products first formed.†

An addition of chlorocarbonic ether to ethylisocyanide has, however, been accomplished, and with the following experiences. Chlorocarbonic ether reacts, already, at ordinary temperatures, on ethylisocyanide and the mixture becomes colored yellow. On heating at 100° , complete reaction takes place in a very short time, but the addition product first formed,



is completely split into carbondioxide, ethylchloride, and ethylisocyanide, $\text{C}_2\text{H}_5\text{N} : \text{C}$, which, generated in the nascent state, mostly polymerizes. Klinger has already observed an entirely analogous decomposition in the case of oxanilethane-imidechloride,



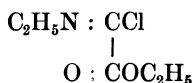
on heating it to 120° .‡

* Ann. Chem. (Liebig), CCLXX. 286-295 and 315.

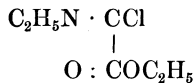
† Ibid., CCLXX. 280, *et seq.* Cf. also Wallach, Ibid., CLXXXIV. 86, 108, CCXIV. 283.

‡ Ibid., CLXXXIV. 283.

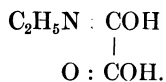
That in the above case an intermediate formation of the imidechloride



takes place was proved as follows. 5 c.cm. ethylisocyanide and 7.8 grams chlorocarbonic ether were heated for 6 hours at 60°–70°, whereby a copious evolution of carbondioxide and of ethylchloride takes place. The very dark residue was treated with absolute ether and much polymerized ethylisocyanide separated out in brown flakes. The ethereal filtrate gave a small amount of an oil (free from chlorocarbonic ether), which was warmed gently with lime water. After getting rid of the excess of lime by means of carbonic acid, the filtrate gave, on concentration, crystals of calcic ethyloxaminic acid, which separated out in needles. The free ethyloxaminic acid obtained from this salt melted at 123°, and was found identical in its properties (as well as also the salt) with the previous statements of Wallach.* The yield of calcic ethyloxaminic acid is very poor,—never over 0.2 gram; its source can only be explained through the intermediate formation of the imidechloride



in the above reaction: this substance must necessarily, by saponification, yield ethyloxaminic acid,

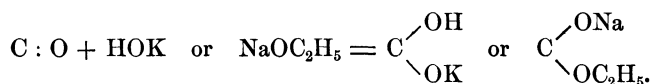


A better yield of the imidechloride could, in all probability, be expected on allowing molecular proportions of ethylisocyanide and chlorocarbonic ether to stand at ordinary temperature for a week or more.

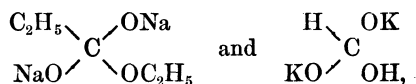
From the above experiments, it is clear that the aliphatic isocyanogen derivatives behave in a manner entirely analogous to the corresponding aromatic derivatives, and differ from these only in the fact that they react more energetically. It was further shown that carbon tetrachloride reacts with ethylisocyanide at 180°, benzolsulphochloride at 85°, benzylchloride at 120°; it was not possible, however, to isolate any definite addition products.

* Ann. Chem (Liebig), CLXXXIV. 58.

It is a noteworthy fact that ethylisocyanide can be heated in a sealed tube for one hour to a temperature of 130° – 170° with sodium ethylate (free from alcohol) without the slightest change. For this reason, it seems to me that in the action of caustic potash or sodium ethylate* on the inert carbonic oxide,† an addition of these reagents to the carbonylgroup‡ must first take place, as follows:



The bivalent carbon atom present in these addition products must, according to the ideas heretofore developed in these Proceedings,§ be far more reactive than the unsaturated carbon atom present in the isocyanides; and, in consequence, a further addition of sodic ethylate or of caustic potash takes place, giving rise to the ortho derivatives,



which naturally, on treatment with water, go over into propionic acid and formic acid salts, respectively.

II. FULMINIC ACID IS IDENTICAL WITH CARBYLOXIME, AND CONTAINS BIVALENT CARBON, $\text{C}:\text{NOH}$.

Formylechloridoxime, $\text{HON}:\text{C}_{\text{Cl}}^{\text{H}}$. The synthesis of fulminate of mercury from sodic nitromethane, described in the preceding paper, leads directly to the conclusion that this substance must be identical with mercuric carbyloxime, $\text{C}:\text{NOhg}$. The behavior of the salt towards concentrated hydrochloric acid is also in favor of this conclusion; there is formed, as Steiner,|| Carstanjen and Ehrenberg,¶ and especially also Divers and Kawakita,** have shown, not a trace of oxalic acid, but only formic acid, corrosive sublimate, and hydroxylamine hydrochloride.

* Berthelot, Ann. Chem. (Liebig), XCVII. 125; Geuther and Fröhlich, Ann. Chem. (Liebig), CCH. 290.

† Ann. Chem. (Liebig), CCLXX. 267.

‡ Ibid., CCLXX. 322.

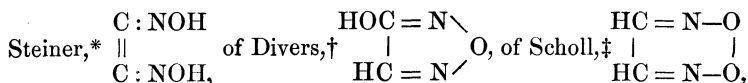
§ Vol. XXVII. pp. 102–104.

|| Ber. de. chem. Ges., XVI. 1484, 2419.

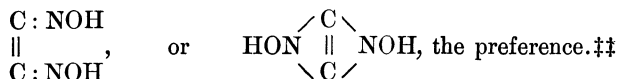
¶ Journ. f. prakt. Chem., [2.], XXV. 232; XXX. 38.

** Journ. chem. Soc., XLV. 13–30, 75.

Notwithstanding this, all the formulæ yet proposed for fulminic acid, as, for example, that of



and many others, have originated from the assumption that this substance contains two carbon atoms in the molecule, because it was regarded as proved by the experiments of Liebig and Gay-Lussac § that the fulminic acid molecule contains two hydrogen atoms possessing entirely different functions. The behavior of mercury fulminate towards bromine || and towards iodine, ¶ whereby products are formed which unquestionably contain two carbon atoms in the molecule, as well as the decomposition of this salt, by means of chlorine, into cyanogen chloride and chlorpicrine,** seem also to be in favor of this conclusion. Only very recently has Scholl †† thought of the possibility of the simple carbyloxime formula, C : NOH, but he still gives the polymerized formula of Steiner,



I have succeeded in proving experimentally, with absolute precision, that fulminic acid is identical with carbyloxime, C : NOH, and that the bivalent carbon atom present in this substance possesses a most surprising and enormous reactivity, so that in all reactions shown by fulminic acid salts the unsaturated carbon atom is the point of attack ; and, since we now possess some light on the nature of bivalent carbon, the entire chemistry of the fulminic acid derivatives is very simply and completely explained, as will become evident from the following experiments.

It has for over seventy years been considered as settled that, on treating fulminic acid salts with dilute hydrochloric acid, a complete destruction of the fulminic acid molecule takes place, and that among

* Ber. d. chem. Ges., XVI. 1484, 2419.

† Journ. chem. Soc., XLV. 21.

‡ Ber. de chem. Ges., XXIII. 3497, 3507.

§ Annales de Chim. et de Phys., XXIV. 294-317, XXV. 285-310.

|| Kekulé, Ann. Chem. (Liebig), CV. 280.

¶ Sell and Biedermann, Ber. d. chem. Ges., V. 89.

** Kekulé, Ann. Chem. (Liebig), CI. 206

†† Ber. d. chem. Ges., XXIII. 3506-3509.

‡‡ Ber. d. chem. Ges., XXIV. 581.

other products prussic acid is set free: this observation has repeatedly been confirmed. *Not a trace of prussic acid is formed, however, but formylchloridoxime*, $\text{HON} : \text{C} \begin{smallmatrix} \text{H} \\ \text{Cl} \end{smallmatrix}$, a substance which, in dilute aqueous solution, — probably because of a slight dissociation into hydrochloric acid and carbyloxim, $\text{C} : \text{NOH}$, — has an odor which cannot be distinguished from that of prussic acid.

This is the reason why, among others,* Liebig and Gay-Lussac, as well as Schischkoff, state that prussic acid is formed in this treatment although, as they themselves add, the presence of prussic acid could not be proved. Gay-Lussac and Liebig write: † “Dans l'intention d'obtenir quelques lumières à cet égard, nous avons essayé d'évaluer la quantité d'acide hydrocyanique qui se dégage lorsqu'on traite le fulminate d'argent par l'acide hydrochlorique, etc. Nous espérions obtenir du cyanur d'argent; mais, à notre grande surprise, il ne s'est fait aucune précipitation, quoique nous nous fussions assurés que la même dissolution d'argent donnait un abondant précipité lorsqu'on y versait de l'acide hydrocyanique.”

Schischkoff says: ‡ “Für das Knallsilber war bereits beobachtet, dass es bei der Einwirkung von Chlorwasserstoffsäure Cyanwasserstoff entwickelt; ich versuchte dieselbe Reaktion mit Knallquecksilber, und war zuerst sehr erstaunt, dass ich nicht ein analoges Resultat nachweisen konnte. Ich schrieb dieses abweichende Verhalten dem Umstande zu, dass sich, in letzterem Falle, ein Quecksilberverbindung von unbekannter Natur bilden möge, welche den Cyanwasserstoff zurückhalten möge. Und, in der That, wenn man vorher etwas schwefelsaures Eisenoxydul der Chlorwasserstoffsäure zusetzt, so lässt sich leicht eine reichliche Entwicklung von Cyanwasserstoff constatiren. Durch das zugesetzte Eisenoxydulsalz wird vermuthlich die den Cyanwasserstoff gebunden zurückhaltende Verbindung zersetzt.”

Formation of Formylchloridoxime from Sodid Fulminate. — The fulminate of mercury used in these experiments was made according to the method of Lobry de Bruyn; § 32 grams of dry salt were regularly obtained from 25 grams of mercury used. Carstanjen and Ehrenberg were the first to show that this salt can be converted quantitatively

* Cf. Ehrenberg, Journ. f. prakt. Chem., [2.], XXV. 241; Scholvien, Ibid., XXXII. 463.

† Annales de Chim. et de Phys., XXV. 308.

‡ Ann. Chem. (Liebig), Suppl. Vol., I. 108.

§ Ber. de chem. Ges., XIX. 1370.

into sodic fulminate by means of sodium amalgam.* It is possible to convert 32 grams of mercury fulminate in 20 minutes into an aqueous colorless solution of sodic fulminate (free from mercury) as follows. The salt is suspended in about 125 c.cm. water and treated with 75 grams of 8 per cent sodium amalgam,† (5 grams more than the theory). The operation is first carried out in a flask, cooling well with water, and then in a flask, having a well fitting glass stopper, taking care to shake thoroughly until the solution contains no mercury.

The sodium fulminate solution thus obtained (about 150 c.cm.) is cooled to 0°, and added slowly, taking care to cool well, to a solution of hydrochloric acid at 0° (114 parts concentrated acid 1.18, and 114 parts water) and thereupon extracting immediately three times with ether. The ethereal solution is placed in a distilling flask and concentrated to one third its volume by distilling off the ether in a stream of dry air at a low temperature (40°), and the solution is then concentrated further at reduced pressure. A very concentrated solution of formylchloridoxime in ether is thus obtained, from which the pure substance is isolated by pouring on a watch-glass and evaporating rapidly in a vacuum desiccator. To insure success in these operations, a very cold winter temperature is essential, and the concentrated ethereal solutions must be kept at 0°. On evaporation of the ether, perfectly transparent very long colorless needles, clear as glass, separate out, which are first transferred to a clay plate (cooled at 0°) and quickly powdered with a platinum spatula, and then weighed as quickly as possible at a low temperature.

0.1235 gram substance, poured directly after weighing into water, and treated with silver nitrate and concentrated nitric acid, gave, after digesting on a water bath, 0.2128 gram AgCl.
0.6585 gram substance gave 1.1006 grams AgCl.

	Theory for CH_2NOCl .		Found.
Cl	44.65		42.63
			41.35

* Journ. f. prakt. Chem., [2.], XXV. 241. Cf. also Scholvien, *Ibid.*, XXXII. 462.

† Sodium amalgam is best made by adding 80 grams sodium to 400 c.cm. toluene in a two-litre flask, and then slowly adding 920 grams of mercury. The toluene heats up to its boiling point, and, after about one half of the mercury has been added, the mass gets solid. The toluene is poured off, the residue melted in a crucible, and then poured out on clay plates. In this way large quantities of sodium amalgam can be made without danger, and with the greatest ease. Cf. Chem. Zeit., 1864, p. 720, and Gmelin, *Kraut*, III. 857.

Preparation of Formylchloridoxime from Silver Fulminate.—Fulminate of silver is best obtained as follows. 5 grams of silver are dissolved in 100 grams nitric acid (sp. gr. 1.34), and the warm solution is poured into 150 c.cm. alcohol (90 per cent) and then heated for 5 to 10 minutes on a water bath until a reaction sets in. The reaction then continues very energetically, of its own accord, and silver fulminate separates out in beautiful needles. The yield is regularly 6.5 grams or more, and the filtrate contains only traces of silver. The salt is much less soluble in boiling water than Liebig states.* In the dry state it is far more dangerous than the mercury salt: it explodes instantly, and with tremendous violence, on touching it very carefully with a platinum spatula. It can, however, be dried without the slightest danger on filter paper, and collected therefrom by means of a camel's hair brush. A silver determination of the salt, dried over sulphuric acid in a vacuum, gave the following result.

0.2013 gram substance, digested with dilute hydrochloric and nitric acids, gave 0.1925 gram AgCl.

	Theory for AgONC.	Found.
Ag	72.00	71.92

In order to convert silver fulminate into formylchloridoxime, 12 grams salt are added to 80 c.cm. hydrochloric acid (one part concentrated acid to one part water) containing pieces of ice, and then, after decanting or filtering from the chloride of silver, proceeding as above in the case of the sodium salt. A small portion of the concentrated ethereal solution of formylchloridoxime was evaporated as above, and the substance immediately analyzed: the chief portion was treated directly with 12.5 grams of aniline (2 molecules) and thus converted smoothly into phenylisuretine (see below).

0.4478 gram substance gave 0.7758 gram AgCl.

	Theory for CH ₂ NOCl.	Found.
Cl	44.65	42.68

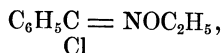
Properties of Formylchloridoxime.—The formylchloridoxime obtained in these two ways is a very reactive and remarkable substance. In the solid condition, or in concentrated ethereal solution, it can be kept at 0° for some time unchanged. It volatilizes very quickly and completely, in small portions, at ordinary temperature, and this serves as a good means of determining its purity. It often happens, when all possible precautions in its manufacture are not observed, that a pro-

* Annales de Chim. et de Phys., XXIV. 297.

duct is obtained which is only partially volatile, and leaves an amorphous opaque residue. This can, however, be seen immediately by the appearance of the formylchloridoxime itself when prepared; if the crystals are clear as glass, the substance is pure; if, on the other hand, the crystals are turbid or opaque, the product is impure. In larger amounts (a few decigrams) formylchloridoxime decomposes very soon at ordinary temperature; it at first becomes colored green, and then puffs up with tremendous evolution of heat and a hissing noise. The same decomposition takes place instantly by the heat of the hand, or on heating the substance in a vacuum at 40°. Carbon monoxide is given off and the puffed up sticky residue consists chiefly of hydroxylamine hydrochloride.

The substance thus possesses a tremendous tendency to decompose into hydrogen chloride and carbyloxime, $C:NOH$, and the latter compound is then split by the hydrochloric acid into carbonmonoxide and hydroxylamine. Formylchloridoxime possesses very poisonous properties, has a very sharp pungent smell, and diluted with air or in dilute aqueous solution has an odor which cannot be distinguished from that of prussic acid; this is probably due to a partial dissociation into hydrogen chloride and carbyloxime, $C:NOH$. Also the action of the substance on the human system, producing a flow of saliva, an irritation in the throat, and violent headaches, is entirely analogous to that of prussic acid. Formylchloridoxime possesses also a very sharp pungent smell, and acts violently on the eyes; the action is not at first very noticeable, but sets in after a time. Thus, for example, after being exposed to the influence of the vapor of the substance for about one hour on an afternoon, my eyes were only colored intensely red, but in the evening a most violent inflammation set in, so that I could hardly see for twenty-four hours. The consequences, however, are only temporary.

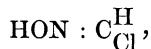
Formylchloridoxime, when brought on the skin, causes white blisters and deep wounds, which heal only very slowly. The substance is not decomposed either by water or by alcohol, — a noteworthy property for a soluble acid chloride; in this respect it resembles the acid chloride, benzenylethoximchloride,



obtained by Tiemann and Krüger,* which is stable even towards caus-

* Ber. d. chem. Ges., XVIII. 732.

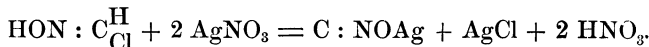
tic potash. The constitution of the substance as formylchloridoxime,



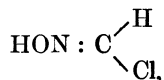
is proved by its behavior towards silver nitrate, ammonia, and especially towards aniline.

Behavior of Formylchloridoxime towards Silver Nitrate.

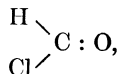
Synthesis of Silver Fulminate, C : NOAg.—On treating an aqueous solution of formylchloridoxime with two molecules of silver nitrate, a quantitative interaction takes place, forming silver fulminate and chloride of silver according to the equation :



This shows what a great tendency exists in this formic acid derivative to split off hydrogen chloride and generate carbyloxime, C : NOH. Some analogous facts to show that this same tendency exists, have already been presented in the previous paper : * whereas the oxime of formylchloride,



can be isolated, formylchloride itself,



does not exist even at 0°, but decomposes spontaneously into hydrogen chloride and into carbon monoxide.

The separation of the chloride of silver and silver fulminate formed in the above reaction can be accomplished very readily. The precipitate, after some standing, and addition of cold dilute nitric acid, is filtered off, well washed, and then boiled out three times with small quantities of aqueous potassic chloride. On cooling, or on concentrating the filtrates, the double salt, AgONC, KONC, discovered by Liebig,† separates out in long glistening flat needles. This salt, after recrystallizing from water, is dissolved in warm water and poured into an excess of cold dilute nitric acid, whereby regenerated silver

* Ann. Chem. (Liebig), CCLXX. 307. 308, 322.

† Annales de Chim. et de Phys., XXIV. 315.

fulminate comes down in very fine colorless needles. Liebig and Gay-Lussac* have regarded this precipitate as "acide fulminique," $C_2HAgN_2O_2$, which is incorrect.

0.2097 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1988 gram AgCl.

	Theory for $AgONC$.	Found.
Ag	72.00	71.37

That silver fulminate, and not "acide fulminique," $C_2HAgN_2O_2$, is always formed on treating the double salt $AgONC$, $KONC$, with nitric acid, was further proved by making the double salt from silver fulminate (made in the ordinary way from silver, nitric acid, and alcohol), and treating it as above, with nitric acid.

0.2129 gram substance, dried over H_2SO_4 in a vacuum, gave 0.2031 gram AgCl.

	Theory for $AgONC$.	Found.
Ag	72.00	71.80

The conclusion of Liebig and Gay-Lussac that the fulminic acid molecule contains two hydrogen atoms, possessing entirely different functions, is therefore not justifiable. In exactly the same way as cyanide of potash gives with silver cyanide a soluble double salt, $AgN : C$, $KN : C$, the entirely analogously constituted silver fulminate gives with potassic fulminate a corresponding double salt, $AgON : C$, $KON : C$. The analogy between the salts of fulminic acid and those of prussic acid is altogether a surprisingly close one, — which can now hardly be considered strange, because both these acids are quite analogous derivatives of isocyanogen. It will be shown further on that a double salt, sodium ferrofulminate, $Na_4Fe(ON : C)_6$, exists, corresponding thus in every respect to the yellow prussiate of soda, sodic ferrocyanide, $Na_4Fe(N : C)_6$. The physiological properties of the soluble prussic acid salts, $MN : C$, and those of the soluble fulminic acid salts, $MON : C$, are so much alike that it is impossible, as far as we now know, to distinguish between them. Schischkoff is only one of the many observers who have worked with salts of fulminic acid who observed the poisonous properties of these salts (the enormous explosive properties are mentioned by all). He remarks:† "Die Knallsäuresalze sind ganz so giftig wie die Cyanmetalle. Die Heftigkeit der Wirkung hängt von der Löslichkeit ab, aber

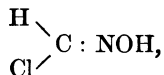
* Annales de Chim. et de Phys., XXIV. 302, XXV. 289.

† Ann. Chem. (Liebig), Suppl. Vol., I. 109.

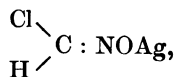
die Vergiftungssymptome sind ganz dieselben wie sie durch die Cyanmetalle hervorgebracht werden. So ist das Knallzink, welches eines der löslichsten unter den Knallsäuresalzen ist, zugleich das giftigste. Ich bemerke noch dass die isocyanursauen Salze [die Fulminurate] gar nicht giftig sind."

E. Davy * first obtained zinc fulminate from mercury fulminate by means of zinc dust and water, and made therefrom, by double decomposition with the metallic hydroxides, many salts of the alkali and alkaline-earth metals. That the majority of these salts are not simple but double salts, e. g. that Davy's baric fulminate is a zinc barium fulminate, $\text{baON} : \text{C}$, $\text{znON} : \text{C}$, was first shown by Fehling. † Ehrenberg is the first who obtained sodic fulminate pure and analyzed the product. ‡

Other Syntheses of Silver Fulminate. — The behavior of silver fulminate towards the calculated amount (one molecule) of dilute hydrogen chloride and of hydrogen sulphide is very remarkable, and is fully cleared up by what follows. On adding one molecule of dilute hydrogen chloride to silver fulminate, suspended in water and kept cold by means of pieces of ice, an energetic reaction immediately takes place, and a strong smell of formylchloridoxime is noticed. The mixture is well stirred, and as soon as it can be filtered clear, this is done. The perfectly clear filtrate is found to contain two substances, formylchloridoxime,



which can easily be extracted from the solution by means of ether, and silver formylchloridoxime,



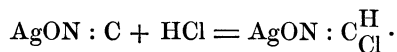
which is soluble in water. The solution, therefore, contains *much chlorine and silver*, which for a long time seemed very enigmatic: on addition of hydrochloric acid, silver chloride is precipitated, and on addition of nitric acid a precipitate consisting of silver fulminate and silver chloride is formed.

* Trans. Roy. Soc. Dublin, 1829; extract in Berzelius's *Jahr.*, XII. 97, 120.

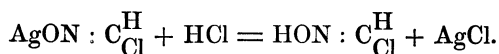
† Ann. Chem. (Liebig), XXVII. 30.

‡ Journ. f. prakt. Chem., [2.], XXXII. 231.

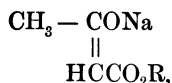
It follows from the above that on treating silver fulminate with dilute hydrochloric acid (one molecule) an addition of hydrogen chloride to the unsaturated carbon atom in this salt takes place,



The addition product, which is soluble in water, is then, in the second stage of the reaction, further acted upon by some of the hydrogen chloride present, and converted partially into silver chloride and formylchloridoxime,

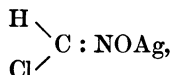


This experiment demonstrates, therefore, in a very pretty manner, that an organic silver salt can react with hydrogen chloride, *leaving the silver present in the molecule entirely intact*. The bivalent carbon atom present in fulminate of silver is so reactive, that the metal is not affected at all. I have already repeatedly, in other cases, drawn attention to similar reactions: the double bond present in sodium acetacetic ether,



is so reactive that, on treatment of this salt with alkyl iodides and acid chlorides,* exclusively or chiefly an addition of these reagents to the double bond takes place, and the sodium atom remains entirely intact in the whole reaction. The same phenomenon has also already been proved to take place with many other silver salts.†

The isolation of the intermediate product,

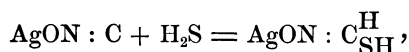


in the above instance therefore furnishes a further very important experimental confirmation of the processes which I have shown take place in the interaction of acetacetic salts with alkyl iodides and acid chlorides. A further entirely analogous example of addition is furnished by the study of the action of hydrogen sulphide on silver fulminate. On adding to silver fulminate, suspended in water con-

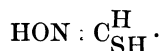
* Ann. Chem. (Liebig), CCLXVI. 52, CCLXX. 331, CCLXXVI. 200.

† Ann. Chem. (Liebig), CCLXX. 329, CCLXXVI. 234, CCLXXVII. 73
Cf. also page 147 of the preceding paper.

taining pieces of ice, an aqueous solution of hydrogen sulphide (one molecule), reaction sets in immediately, and a strong odor resembling very closely that of prussic acid is noticed. The clear colorless filtrate contains both *silver and sulphur*; on addition of silver nitrate, a brown precipitate consisting of silver fulminate and silver sulphide is obtained; hydrochloric acid precipitates chloride and sulphide of silver. On treating silver fulminate with hydrogen sulphide, an addition must therefore take place as follows:

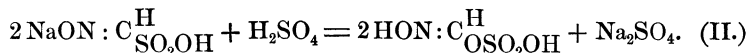
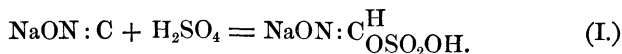


forming silver thioformhydroxamate, which, like silver formylchlorid-oxime, is soluble in water; this salt is then further acted upon by hydrogen sulphide, and partially converted into silver sulphide and thioformhydroxamic acid,



The above facts suffice also to explain fully the former experiments of Ehrenberg* and of Scholvien.† Scholvien believed he had obtained free fulminic acid on adding aqueous sodic fulminate to cold dilute sulphuric acid and extracting *immediately* with ether, for he obtained by shaking the ethereal solution quickly with silver nitrate a precipitate of silver fulminate.‡ He describes the "free fulminic acid" as a volatile compound, which affects the eyes and mucous membrane of the nose in an intolerable manner.

It is now clear that Scholvien's compound was nothing else than formylsulphate-oxime, $\text{HON} : \text{C}_{\text{OSO}_2\text{OH}}^{\text{H}}$, formed by an addition of sulphuric acid to the unsaturated carbon atom present in sodic fulminate, as follows:



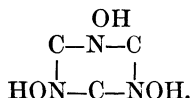
Formylsulphate-oxime is a substance which is far less stable than the analogous formylchloridoxime described above, which is not surprising. It possesses, just as formylchloridoxime, only to a far greater extent, a tendency to split into sulphuric acid and carbyl-oxime, $\text{C} : \text{NOH}$. This is the reason why Scholvien always noticed

* Journ. f. prakt. Chem., [2.], XXX, 43.

† Ibid., XXXII., 463, 481.

‡ Ibid., XXXII. 463, 480.

in an ethereal solution of the substance after a few moments a rise in temperature, "which often is so great that the ether begins to boil." * The carbyloxime formed in the nascent state polymerizes to a great extent, just as has often been noticed in analogous cases with isocyanides. For this reason it seems to me highly probable that Scholvien's isocyanuric acid † consists simply of polymerized carbyloxime, and probably possesses the constitution



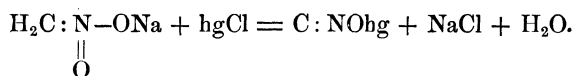
All the properties of the substance can easily be explained by this formula, and a further study of it will be taken up very shortly; especially also because Scholvien states that on treating the silver salt $\text{C}_3\text{HN}_3\text{O}_3\text{Ag}_2$ with ethyl iodide, "a filtrate was obtained smelling strongly of carbylamine." ‡ It is very likely that in this reaction no ethyl isocyanide, but ethylcarbyloxime, $\text{C}_2\text{H}_5\text{ON}:\text{C}$, is formed, — a substance which, as will be shown farther on, cannot be distinguished from ethylisocyanide in respect to odor.

Ehrenberg has already had an ethereal solution of formylchlorid-oxime (containing also mercuric chloride and hydrogen chloride) in his hands. He obtained it by passing dry hydrogen chloride over mercuric fulminate suspended in absolute ether; and he assumes that free fulminic acid may possibly be present in the solution. He describes the ethereal solution § as a "strong-smelling liquid, bringing tears to the eyes, and affecting the mucous membrane, and causing an intensely bitter taste in the mouth. The smell reminds one of prussic acid, but this could not be detected in the solution. On attempting to distil off the ether, the mass all at once decomposed with violence and with a hissing noise."

Ehrenberg was, in consequence, unable to isolate the product, and studied only the action of aqueous ammonia upon the ethereal solution of the substance. The nature of the compounds which he obtained in this way is cleared up by the experiments mentioned below.

Fulminic acid salts can therefore be obtained synthetically in four different ways, as follows.

1. From sodic nitromethane:



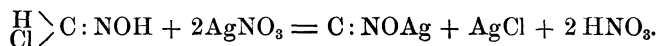
* Journ. f. prakt. Chem., [2.], XXXII. 463.

† Ibid., XXXII. 464.

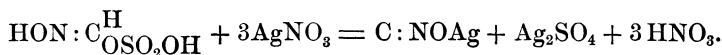
‡ Ibid., XXXII. 473.

§ Ibid., XXX. 44

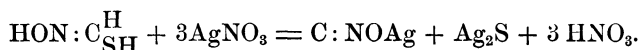
2. From formylchloridoxime :



3. From formylsulphate-oxime :

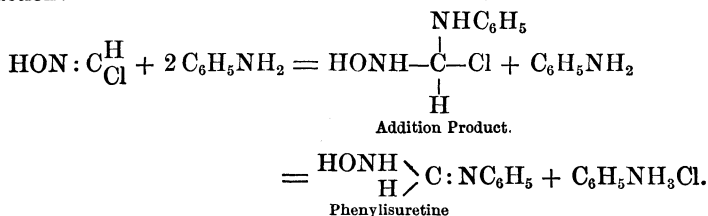


4. From thioformhydroxamic acid :

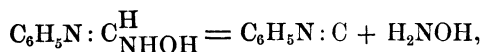


Behavior of Formylchloridoxime towards Aniline.

The constitution of formylchloridoxime is proved by the fact that aniline coverts it quantitatively into phenylisuretine, according to the reaction :



On adding an ethereal solution of aniline (2 molecules, 12.5 grams) to a concentrated ethereal solution of formylchloridoxime (obtained from 12 grams silver fulminate), a clear solution at first takes place, but very soon a white salt begins to separate out in large quantity. After standing for one hour, much ether is added, and the salt filtered off. The residue, 9.2 grams, consists of a mixture of aniline hydrochloride and phenylisuretine, which, since the latter substance is insoluble in cold water, can readily be separated. The ethereal filtrate gives, on evaporation, phenylisuretine and traces of aniline. Altogether 6.5 grams of phenylisuretine were obtained. It is purified by crystallizing from ether, and obtained in flat colorless needles, melting with decomposition at 138°. The substance crystallizes from water in long fibrous colorless needles, or, if the solution is dilute, in leaflets. A slight decomposition into phenylisocyanide and hydroxylamine, according to the equation,



always takes place on recrystallizing the substance from water. Phenylisouretine shows altogether a great tendency to decompose in this manner. On melting the solid substance, a strong smell of phenylisocyanide is noticed; also on warming with sodic hydrate, in which it first dissolves. The compound possesses strong basic properties, and dissolves immediately in cold dilute acids. It gives a deep purple red coloration with ferric chloride, and reduces silver solutions on warming. Because of its decomposition into phenylisocyanide, the substance burns with great difficulty.*

0.1435 gram substance, dried over H_2SO_4 in a vacuum, gave 0.3202 gram CO_2 and 0.0799 gram H_2O .

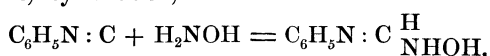
0.1549 gram substance, dried over H_2SO_4 in a vacuum, gave 0.3452 gram CO_2 and 0.0848 gram H_2O .

0.1526 gram substance, dried over H_2SO_4 in a vacuum, gave 0.3428 gram CO_2 and 0.0843 gram H_2O .

0.1544 gram substance gave 28.5 c.cm. N_2 at 20° and 755 mm.

	Theory for $\text{C}_7\text{H}_8\text{N}_2\text{O}$.		Found	
C	61.76	60.87	60.78	61.27
H	5.89	6.18	6.08	6.14
N	20.59	20.97		

In order to prove absolutely that the substance was really phenylisouretine it was necessary to obtain it synthetically from a formic acid derivative. To effect this, two ways were open; the substance could, in the first place, easily be formed from phenylisocyanide and hydroxylamine, by addition,



In the second place, it could probably easily be obtained from isouretine by means of aniline hydrochloride.

The second method was first chosen, and since this succeeded directly and quantitatively, the first way, which in all probability would also yield phenylisouretine, was not tried.

Preparation of Isouretine, $\text{HN}:\text{C} \begin{smallmatrix} \text{H} \\ \text{NHOH} \end{smallmatrix}$. — Lossen and Schifferdecker have obtained this compound from prussic acid and hydroxylamine.† The following slight modification of their method gives a very good yield of isouretine. A solution of 30 grams of cyanide of

* Ann. Chem. (Liebig), CCLXX. 276.

† Ibid., CLXVI. 295.

potash in 60 grams of water, is added to a solution of 31.5 grams hydroxylaminehydrochloride (one molecule) in 60 c.cm. water; great care must be taken that the temperature never rises above 5° . The solution is kept for 48 hours at 5° , and then allowed to evaporate spontaneously in flat dishes. The dry residue is boiled out with absolute alcohol, and on cooling and evaporating the filtrates, isuretine separates out in colorless needles, melting at 114° – 115° . The last portions separating out are best crystallized from acetic ether, from which the substance is obtained perfectly pure and beautifully crystallized. With the exception of the melting point (Lossen and Schiffer-decker give mpt. 104° – 105°), the former statements concerning its properties could be confirmed.

The yield is 84 grams pure isuretine from 142 grams cyanide of potash used.

0.2531 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1872 gram CO_2 and 0.1571 gram H_2O .

0.1369 gram substance, dried over H_2SO_4 in a vacuum, gave 56.7 c.cm. N_2 at 21° and 753 mm.

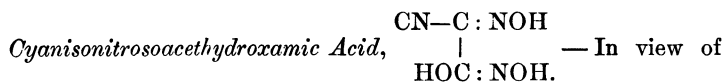
	Theory for $\text{CN}_2\text{H}_4\text{O}$.	Found.
C	20.00	20.17
H	6.67	6.89
N	46.67	46.71

Phenylisuretine from Isuretine. — On heating isuretine (1 gram) and aniline hydrochloride (one molecule) in alcoholic solution, an interaction with formation of phenylisuretine and ammonium chloride very soon takes place. After distilling off the alcohol, and treating the residue with cold water to get rid of ammonium chloride, it is crystallized from ether; 1.7 grams of phenylisuretine were obtained, crystallizing in flat needles, melting at 138° , and in every respect identical with the compound obtained from formylchloridoxime.

0.0687 gram substance, dried over H_2SO_4 in a vacuum, gave 13 c.cm. N_2 at 24° and 755 mm.

	Theory for $\text{C}_7\text{H}_8\text{N}_2\text{O}$.	Found.
N	20.59	21.07

Behavior of Formylchloridoxime towards Ammonia.



the results with aniline, it was at first expected that, on treating for-

mylchloridoxime with ammonia, isuretine and ammonium chloride would be formed. The reaction takes place, however, in a different manner, no matter whether the ethereal solution of formylchloridoxime is treated with concentrated aqueous, or with dry gaseous ammonia. It is best to proceed as follows. The ethereal solution, obtained by extracting the acidified sodium fulminate solution, is treated directly, without concentrating it, in a separatory funnel with small quantities of concentrated aqueous ammonia (30 per cent), taking care to shake well and to cool thoroughly with water. A yellow powder separates out in large quantity, which settles on shaking in the lower portion of the funnel. A portion from 32 grams of mercuric fulminate was always worked up at a time, and about 40–50 c.cm. concentrated ammonia used (until a strong smell of ammonia is apparent). The aqueous solution with the yellow powder suspended in it, is then drawn off and filtered, and the filtrate again brought into the separatory funnel, and the operation repeated until all the yellow powder is brought on the filter; it is then dried on clay plates. The filtrate contains much ammonium chloride and also some of the yellow substance, which is sparingly soluble in cold water. 25 grams of the yellow powder were regularly obtained from 96 grams of mercury fulminate: it consists of the secondary ammonium salt of cyanisonitrosoacethydroxamic acid; it cannot be crystallized from hot water however without some decomposition. The yellow powder is therefore converted directly into the free acid. 25 grams of the salt are suspended in 40 c.cm. water, and 120 c.cm. dilute hydrochloric acid (16.5 per cent) added, and thereupon the resulting solution is extracted 35 times with ether. After drying with chloride of calcium, the ethereal solution is distilled off and 15 grams of a colorless solid remains, which already consists of practically pure cyanisonitrosoacethydroxamic acid. The substance is recrystallized from ether with addition of a small amount of ligroine (bpt. 70°–80°), and obtained in colorless cubes or in 4-sided prisms, clear as glass, and melting, with decomposition, at 117°–118°.

0.1555 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1490 gram CO_2 and 0.0438 gram H_2O .

0.1125 gram substance, gave 30.5 c.cm. N_2 at 20° and 751 mm.

	Theory for $\text{C}_3\text{H}_3\text{N}_3\text{O}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$.	Found.
C	26.09	26.13
H	2.90	3.13
N	30.43	30.64

The substance is readily soluble in water, and in organic solvents with the exception of benzene and ligroine. It crystallizes from acetic acid in transparent quadratic pyramids with basal planes. The substance has a strong acid smell, and gives both primary and secondary salts, which are colored yellow. An aqueous solution of the acid gives with ferric chloride an intense blood-red coloration.

Primary Silver Salt, $C_3H_2N_3O_3Ag$. — This salt separates out slowly in yellow flat prisms on addition of silver nitrate (one molecule) to a concentrated aqueous solution of the acid. The filtrate gives, on long standing, a brownish red precipitate.

0.1948 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1172 gram $AgCl$.

	Theory for $C_3H_2N_3O_3Ag$.	Found.
Ag	45.76	45.29

Secondary Potassium Salt, $C_3HN_3O_3K_2 \cdot H_2O$. — This salt is obtained quantitatively on adding an alcoholic solution of the acid to an alcoholic solution of potassic hydrate (two molecules). It separates out as a yellow crystalline powder, which, after being well washed with alcohol and dried over sulphuric acid in a vacuum, was analyzed.

0.2038 gram substance gave 0.1596 gram K_2SO_4 .

	Theory for $C_3HN_3O_3K_2H_2O$.	Found.
K	34.98	35.11

Behavior of the Acid towards Ammonia. — On adding concentrated ammonia solution to an aqueous solution of cyanisonitrosoacethydroxamic acid, the secondary ammonium salt separates out as a yellow amorphous powder, identical with the salt obtained directly from formylchloridoxime and ammonia. If, however, much ammonia solution is used, a yellow solution results, in which, after some standing, no longer the original substance, but its decomposition products are present. These are the products which Ehrenberg (see above) obtained on treating his ethereal formylchloridoxime solution with a large quantity of aqueous ammonia. The primary product of the reaction, the ammonium salt of cyanisonitrosoacethydroxamic acid, was obtained by him only in traces, and was not further investigated.* It simply remained dissolved in the aqueous ammonia solution, because he used a very large amount of the solution. He obtained, on allowing this solution to stand in the air, three compounds. First, a substance,† $C_3H_4N_4O_2$, which separates out in yellow needles; on

* Journ. f. prakt. Chem., [2.], XXX. 47.

† Ibid., XXX. 49.

acidifying and extracting with ether, two other compounds were obtained: one of these, which is far less soluble in cold ether, he calls isofulminuric acid,* and its composition as $C_3H_3N_3O_3$ was determined by many analyses; the other substance was a syrupy acid from which he obtained a small amount of a crystallized ammonium salt, $C_3H_7N_5O_3$.†

These three substances are all obtained by allowing an ammoniacal solution of pure cyanisonitroacethydroxamic acid to stand in the air, and proceeding according to the directions of Ehrenberg. It is to be noted that Ehrenberg's compound of the formula $C_3H_4N_4O_2$ possesses weak acid as well as also strong basic properties; it dissolves therefore instantly in cold dilute hydrogen chloride. It also gives with ferric chloride an intense blood-red coloration.

Behavior of Cyanisonitrosoacethydroxamic Acid towards Water.—Whereas a solution of the free acid in concentrated hydrochloric acid or in concentrated sulphuric acid can be kept without essential change for twelve hours in the cold, an aqueous solution of the acid (2 grams) is completely decomposed after two hours heating on a water bath. The solution no longer gives a yellow but a white precipitate with silver nitrate. On extracting with ether, and drying the ethereal solution with calcic chloride, two substances are obtained which are identical with Ehrenberg's isofulminuric acid and his syrupy acid. The former can easily be separated from the latter by washing with a small amount of ether. It was crystallized (1 gram) from a small amount of water, and obtained as a white spongy powder identical in its properties and its behavior with Ehrenberg's isofulminuric acid. The fact that the substance gives with ferric chloride a deep blood-red coloration is worthy of mention.

0.1687 gram substance, dried at 100° , gave 0.1725 gram CO_2 and 0.0386 gram H_2O .

0.0780 gram substance, dried at 100° , gave 23 c.cm. N_2 at 22° and 750 mm.

	Theory for $C_3H_3N_3O_3$.	Found.
C	27.91	27.89
H	2.33	2.54
N	32.56	32.94

The syrupy acid which is formed at the same time is identical with the corresponding compound obtained by Ehrenberg, but for the present has not been further studied.

* Journ. f. prakt. Chem., [2.], XXX. 55.
VOL. XXX. (N. S. XXII.)

† Ibid., XXX. 59.

Behavior of the Acid $C_3H_3N_3O_3, \frac{1}{2} H_2O$, *towards concentrated Caustic Potash.* — In the expectation that cyanisonitrosoacethydroxamic acid must, by treatment with caustic potash, yield potassic isonitrosomalonnate, it was heated (1 gram) with concentrated potassic hydrate (6.9 grams KOH and 10 grams water) for three quarters of an hour on a water bath. Ammonia is given off copiously, and the solution is then treated further according to the method of Baeyer.* On addition of alcohol to the solution, acidulated with acetic acid, an oily precipitate is obtained, which, on rubbing with a glass rod, solidifies. Recrystallized once from water and alcohol, it is obtained (0.5 gram) in colorless leaflets, which give with ferric chloride a deep red coloration, and which resemble very closely potassic isonitrosomalonnate. The analysis of the salt, dried over sulphuric acid in a vacuum, showed, however, that another substance is at hand, and that the original acid has lost *only one atom of nitrogen* as ammonia in the above treatment.

0.2498 gram substance gave 32.5 c.cm. N_2 at 20° and 746 mm.

0.0204 gram substance gave 0.0988 gram K_2SO_4 .

	Theory for $C_3HN_2O_4K, H_2O$.	Found.
N	15.04	14.61
K	21.04	21.89

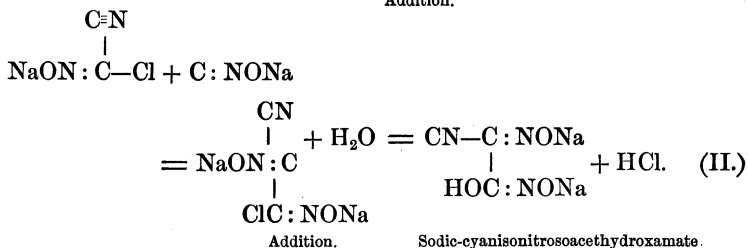
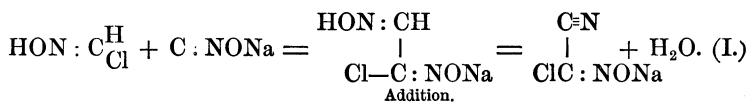
Behavior of the Acid $C_3H_3N_3O_3, \frac{1}{2} H_2O$, *towards concentrated Hydrogen Chloride.* — 2 grams of the acid are heated in a sealed tube for five hours with concentrated hydrochloric acid (10 c.cm. of sp. gr. 1.18). On opening the tube, the presence of carbon dioxide was noticed; and on evaporating the contents on a water bath, 2.5 grams of residue are regularly obtained. On digesting this with ether, the oxalic acid formed in the reaction (proved by its tests and properties) was removed, and the residue (2 grams) consists of a mixture of much ammoniac chloride and of little hydroxylamine hydrochloride. A quantitative determination, carried out by means of Fehling's solution, showed that the residue (2 grams) consists of 1.6 grams ammonium chloride and of 0.4 grams hydroxylamine hydrochloride.

It follows from these experiments that cyanisonitrosoacethydroxamic acid is decomposed by hydrogen chloride into oxalic acid, carbon dioxide, ammonium chloride, and oxyammonium chloride; and that more than two thirds of its nitrogen is eliminated in the form of ammoniac chloride.

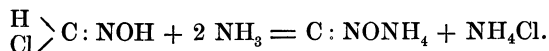
* Ann. Chem. (Liebig), CXXXI. 292.

The Constitution of the Acid. — That the acid, $C_3H_3N_3O_3, \frac{1}{2} H_2O$, obtained from formylchloridoxime by means of ammonia, is identical with cyanisonitrosoacethydroxamic acid cannot at present be determined with certainty from its decomposition products. The constitution of the acid as given is however extremely probable *because of its quantitative formation* from sodic fulminate (two molecules) and formylchloridoxime.

The action of formylchloridoxime on sodic fulminate can, because of the entirely analogous results obtained with phosgene on isocyanides,* take place only in the following manner.

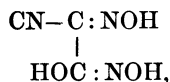


The reaction which takes place on treating formylchloridoxime with ammonia is entirely analogous: a decomposition of the formylchloridoxime into ammonium chloride and ammonic fulminate first takes place as follows:

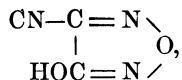


The ammonic fulminate thus formed (two molecules) then reacts with unchanged formylchloridoxime (just as in the above equations does sodic fulminate) and ammonic cyanisonitrosoacethydroxamate is formed.

As can easily be seen, cyanisonitrosoacethydroxamic acid,

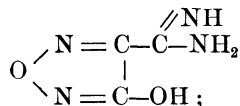


can readily go over by loss of water into a furazane derivative,

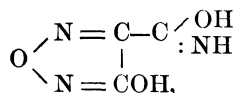


* Ann. Chem. (Liebig), CCLXX. 286, 315.

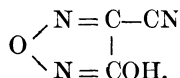
and this suffices to explain fully all the reactions and decomposition products of this acid. That the furazane ring is a very stable one is clearly evident from the experiments of Wolff.* Ehrenberg's product, $C_3H_4N_4O_2$, is therefore very probably



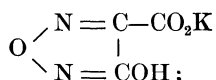
his isofulminuric acid is identical with oxyfurazane-carbonicamide,



whereas the syrupy acid obtained by him is probably oxyfurazane-cyanide,

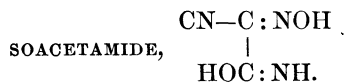


The product obtained by myself, by means of concentrated potassic hydrate, $C_3HN_2O_4K$, H_2O , is, on the other hand, probably identical with potassic oxyfurazanecarboxylate,



it must therefore be obtained from all three of Ehrenberg's compounds by saponification. Further experiments, with a view of proving more sharply the constitution of these decomposition products of cyanisonitrosoacethydroxamic acid, will be taken up again shortly.

III. DESOXYFULMINURIC ACID IS IDENTICAL WITH CYANISONITRO-



Liebig† and Schischkoff‡ have shown that on boiling mercuric fulminate with ammoniac chloride, or with potassic chloride and water, a monobasic acid, $HC_3H_2N_3O_3$, is formed which, at present, is known by the name of fulminuric acid. Ehrenberg§ obtained the same acid

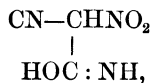
* Ann. Chem. (Liebig), CCLX. 101. Cf. Ber. d. chem. Ges., XXIV. 1167.

† Ann. Chem. (Liebig), XCV. 282.

‡ Ibid., XCVII. 53, CI. 213.

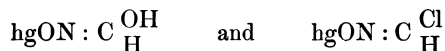
§ Journ. f. prakt. Chem., [2.], XXXII. 98.

by boiling fulminate of mercury with water. Among the many formulæ which have been advanced as representing the constitution of this acid, the one proposed by Steiner,*



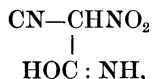
possesses the greatest probability. It explains very simply the formation of nitroacetonitrile, $\text{CN—CH}_2\text{NO}_2$, from it by means of sulphuric acid,† as well as the formation of trinitroacetonitrile, $\text{CN—C(NO}_2)_3$, by means of sulphuric acid and nitric acid.‡

It follows directly from the above experiments, that, on boiling mercuric fulminate with water and either ammoniac chloride or potassic chloride, an addition of water or of hydrogen chloride to the unsaturated carbon atom present in this salt must at first take place, and thus the products



must be formed. These can then act further, in the second stage, on unchanged mercuric fulminate in exactly the same way as formylchloridoxime acts on sodic fulminate (see above). It was therefore suspected for a long time that cyanisonitrosoacethydroxamic acid must be an intermediate product in the formation of fulminuric acid (its isomer). After, however, many fruitless attempts were made to convert this substance into fulminuric acid, by oxidation, by boiling with mercuric oxide, or with ammonia and oxide of mercury, etc., it seems to me impossible that this is formed as an intermediate product.

If fulminic acid is identical with nitrocyanoacetamide,



and this is proved to be the case farther on, it must be formed from mercury fulminate in a manner entirely analogous, for instance, to the formation of mesoxanilide from phenylisocyanide, phosgene, and water,§ or also to that of cyanisonitrosoacethydroxamic acid from formylchloridoxime and soluble fulminic acid salts. The following explanation of the reaction which takes place in the formation

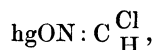
* Ber. d. chem. Ges., IX. 784.

† Steiner, Ber. d. chem. Ges., IX. 782.

‡ Schischkoff, Ann. de Chim. et de Phys., [3.], XLIX. 310.

§ Ann. Chem. (Liebig), CCLXX. 291.

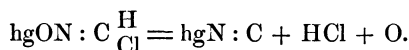
of fulminuric acid seems to me at present to be the most plausible one. The product first formed by the action of ammoniac chloride on mercury fulminate,*



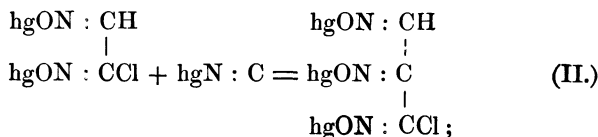
reacts first on the unchanged salt, giving by addition



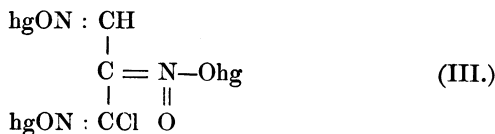
Mercury formylchlorid-oxime is, however, as is readily understood and has also been proved,† a strong oxidizing agent, which can easily go over, with loss of oxygen, into cyanide of mercury,



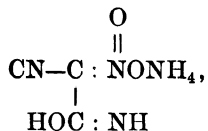
The cyanide of mercury thus formed, can then react with the addition product (I.) as follows :



and this product is then oxidized to



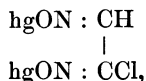
from which, by means of ammonia, the ammonium salt of fulminuric acid,



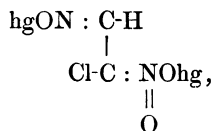
* The reaction with water is entirely analogous; it is only necessary to substitute OH for Cl.

† An aqueous solution of formylchloridoxime oxidizes, for example, ferrous salts in acid solution immediately in the cold, and prussic acid is set free. Cf. also Schischkoff, Ann. Chem. (Liebig), Suppl. Vol., I. 108.

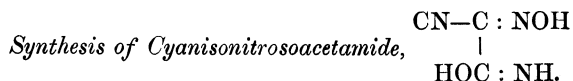
can readily be formed. It is, however, also possible that the addition product I.,



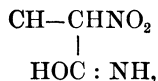
first goes over, by oxidation, into



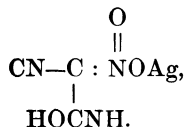
which then can add itself to cyanide o. mercury, $\text{C} : \text{Nhg}$, present, giving directly the addition product III., which, with ammonia, gives mercuric oxide and ammoniac fulminate.



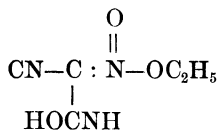
Seidel * has recently obtained, on treating silver fulminate with ethyl iodide, a substance, $\text{C}_3\text{H}_2\text{N}_3\text{O}_3(\text{C}_2\text{H}_5)$, which, on boiling with water, decomposes into acetaldehyde, $\text{C}_2\text{H}_4\text{O}$, and a substance having the formula $\text{C}_3\text{H}_3\text{N}_3\text{O}_2$, which he therefore calls desoxyfulminuric acid. If fulminuric acid is identical with nitrocyanoacetamide,



it follows, by reason of the experiments on nitro compounds presented in the preceding paper, that, on treating the silver salt of fulminuric acid,



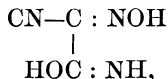
with ethyl iodide, an ester of the constitution



must be formed.

* Ber d. chem. Ges., XXV. 431 and 2756.

This ester must then, on boiling with water, be split by intra-molecular oxidation into cyanisonitrosoacetamide,



and into acetaldehyde, $\text{CH}_3\text{CH} : \text{O}$. These considerations lead to the conclusion that desoxyfulminuric acid must be identical with cyanisonitrosoacetamide, and the following experiments, which have led to a synthesis of this compound, prove that in fact both products are absolutely identical.

Cyanisonitrosoacetic ether, as well as cyanisonitrosoacetic acid, have recently been obtained by Muller* from cyanacetic ether. I also have made both these compounds in this way, and can confirm the statements of Muller completely, except that the melting point of cyanisonitrosoacetic ethylester was found to be 133° instead of 128° – 129° , when the substance is crystallized from benzene. Both compounds were analyzed, and gave figures agreeing well with the theoretical ones. It is somewhat noteworthy that the ester melts higher than the free cyanisonitrosoacetic acid.

On heating cyanisonitrosoacetic ethylester (2 grams) in a sealed tube with 10 c.cm. of alcoholic ammonia for four hours at 100° , a salt separates out, on cooling, in yellow heavy nodules. It is filtered off, well washed with alcohol, dissolved in hydrochloric acid, and extracted with ether. After drying the ethereal solution with calcic chloride, and concentrating, colorless heavy plates separate out, which, recrystallized once more from ether, melt at 184° and are perfectly pure.

0.1997 gram substance, dried over H_2SO_4 in a vacuum, gave 0.2325 gram CO_2 and 0.0520 gram H_2O .

0.1515 gram substance, gave 50.2 c.cm. N_2 at 19° and 744 mm.

	Theory for $\text{C}_3\text{H}_3\text{N}_3\text{O}_2$.	Found.
C	31.86	31.75
H	2.66	2.89
N	37.17	37.27

The substance crystallizes either in needles, or in heavy many-sided flat crystals, and is identical in every respect with Seidel's desoxyfulminuric acid. In order to be absolutely certain, this substance was made according to Seidel's directions, and compared in every detail with the synthetic product; no difference could be de-

* Annales de Chim. et de Phys., [7.], I. 504.

tected between them. Furthermore, desoxyfulminuric acid made from mercury fulminate is converted quantitatively into cyanisonitrosoacetic acid and into isonitrosomalonic acid, as is evident from the following experiments.

3 grams desoxyfulminuric acid were heated on a water bath for one hour with 2.2 grams sodic hydrate and 40 c.cm. water, whereby a copious evolution of ammonia was noticed; the solution was acidified with dilute sulphuric acid, and extracted with ether. After evaporating the ether, the residual oil (1.6 grams) slowly solidifies. It was twice crystallized from a mixture of ether and benzene, and obtained in colorless needles, melting at 103° . The substance was identical with cyanisonitrosoacetic acid prepared from cyanacetic ether.*

0.2048 gram substance, dried over H_2SO_4 in a vacuum, gave 0.2190 gram CO_2 and 0.0495 gram H_2O .

0.1251 gram substance gave 25.2 c.cm. N_2 at 19° and 752 mm.

	Theory for $\text{C}_3\text{H}_2\text{N}_2\text{O}_3, \frac{1}{2} \text{H}_2\text{O}$.	Found.
C	29.27	29.16
H	2.44	2.68
N	22.76	22.97

It is noteworthy that cyanisonitrosoacetic acid, which has now been obtained in four different ways,† always contains half a molecule of crystal water.

0.8 gram desoxyfulminuric acid, 2.5 grams caustic potash, and 5 c.cm. water, were heated for 3 hours on a water bath, and then worked up according to the method of Baeyer‡ for potassic isonitrosomalonnate. The salt was recrystallized twice, and 0.95 gram was obtained. The analysis agrees with theory for anhydrous salt.

0.2250 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1844 gram K_2SO_4 .

0.2520 gram substance gave 16 c.cm. N_2 at 24° and 744 mm.

0.3030 gram substance gave 0.1906 gram CO_2 and 0.0175 gram H_2O .

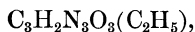
	Theory for $\text{C}_3\text{HO}_5\text{K}_2\text{N}$	Found.
C	17.22	17.15
H	0.48	0.64
N	6.70	6.96
K	37.32	36.74

* Annales de Chim. et de Phys., [7.], I. 504.

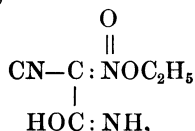
† Ann. Chem. (Liebig), CXXXI. 295.

‡ Wolff and Gans, Ber. d. chem. Ges., XXIV. 1169; Söderbaum, Ber. d. chem. Ges., XXIV. 1231 and 1989; Muller, Annales de Chim. et de Phys., [7.], I. 504.

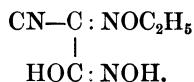
Seidel obtained by heating silver fulminurate* with ethyl iodide at 100°, instead of at 80°, a second compound of the formula,



melting point 155°.† This is in all probability formed from the normal and original ester,



by a molecular rearrangement, especially since we now know that such esters are unstable compounds, capable of intramolecular oxidation. It is very probable that this second compound, $\text{C}_8\text{H}_2\text{N}_8\text{O}_8(\text{C}_2\text{H}_5)$, possesses the constitution

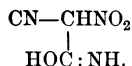


It is a strong acid, — a fact which Seidel does not mention.

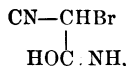
IV. SODICFERROFULMINATE, $\text{Na}_4\text{Fe}(\text{ON}:\text{C})_6 + 18 \text{H}_2\text{O}$.

The remarkable resemblance of fulminic acid, $\text{C}:\text{NOH}$, and its salts, $\text{C}:\text{NOM}$, to prussic acid, $\text{C}:\text{NH}$, and its salts, $\text{C}:\text{NM}$, has become very evident by reason of the facts presented above. This resemblance is so great, that many observers have been led astray in working with fulminic acid compounds. For this reason it seems to me that *no longer the slightest doubt can exist* concerning the nature of prussic acid and its salts.‡ *They are unquestionably all derivatives of isocyanogen,*

* It need hardly be mentioned that many fruitless experiments were carried out in the hope of synthesizing fulminuric acid, which, according to the above results, must be identical with nitrocyanoacetamide,



Bromcyanoacetamide,



mpt. 122°, can easily be made from cyanoacetamide, bromine, and water, but all attempts to convert it, by means of potassic or silver nitrite, into nitrocyanoacetamide were attended with negative results.

† Ber. d. chem. Ges., XXV. 2756.

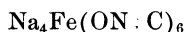
‡ Ann. Chem. (Liebig), CCLXX. 329.



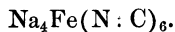
and not, as has so long been supposed, derivatives of cyanogen,



The analogy between fulminic acid and prussic acid is further shown by the isolation of a double salt, sodic ferrofulminate,



corresponding completely with sodic ferrocyanide,



Carstanjen and Ehrenberg have already drawn attention to the very peculiar behavior of sodic fulminate towards iron salts, and shown that solutions result in which the presence of iron can no longer be detected.*

On adding to an aqueous solution of sodic fulminate containing some sodic hydrate, and obtained as stated above from mercuric fulminate (32 grams), a solution of ferrous sulphate (one molecule to six molecules sodic fulminate), a yellowish solution is obtained, in which the presence of iron cannot be detected either by means of sodic hydrate or of ammonium sulphide. The filtered solution is allowed to evaporate spontaneously in flat dishes in the air, and after some time beautiful yellow needles, often over an inch in length, separate out. It is easily possible to obtain 11 grams of this substance in a perfectly pure state from the above amount of mercury fulminate taken. The crystals are filtered off, washed with a small amount of cold water, and then dried between filter paper; they do not contain a trace of sodium sulphate.

On further evaporation of the mother liquors, more of the salt separates out, but mixed with Glauber's salt. The sodic ferrofulminate thus obtained is freely soluble in cold water, and gives with ferric chloride an intense purple-red coloration, which is incredibly delicate. The pure substance is, however, unstable in aqueous solutions or in a moist condition, and soon gets colored purplish red; the presence of sodic hydrate increases its stability, and for this reason it is well to recrystallize in the presence of a small amount of sodic hydrate. The

* Journ. f. prakt. Chem., [2.], XXV. 246, 247.

salt contains 18 molecules of crystal water, a portion of which goes off quickly in the air or over sulphuric acid in a vacuum, and the substance changes its color first to white and then slowly to red. A concentrated aqueous solution of the salt is precipitated by alcohol, first in yellow needles, and on addition of more alcohol these are suddenly transformed into a colorless white powder with loss of a portion of the crystal water.

Whereas, the double salt, $\text{AgON}:\text{C}$, $\text{KON}:\text{C}$, is far more stable than the corresponding prussic acid double salt, $\text{AgN}:\text{C}$, $\text{KN}:\text{C}$, in this case the ferrofulminate of soda is far less stable than the analogous sodic-ferrocyanide. It does not give an acid, ferrofulminic acid corresponding to ferrocyanic acid, and, even on losing its crystal water, the salt $\text{Na}_6\text{Fe}(\text{ON}:\text{C})_6 + 18 \text{H}_2\text{O}$ dissociates completely into sodic fulminate, $\text{NaON}:\text{C}$, and into ferrous fulminate, $\text{Fe}(\text{ON}:\text{C})_2$.

On treating the salt in the cold with dilute hydrochloric acid, it is converted into formylchloridoxime. Also on boiling it in aqueous solution with sodic hydrate or with ammonium sulphide, it is slowly decomposed, with separation of iron hydrate or iron sulphide.

An aqueous solution of the salt gives with lead acetate, silver nitrate, or mercuric chloride, white very explosive precipitates, which appear to consist exclusively of the corresponding fulminic acid salts.

As mentioned above, the yellow salt easily loses a portion of its crystal water and becomes colored white; on addition of water, it is again transformed completely into the original salt. After long standing over sulphuric acid in a vacuum, the white salt becomes tinged red, and finally is converted into a red powder, which no longer consists of ferrofulminate of soda, but of a mixture of sodic fulminate and ferrous fulminate; it then dissolves only partly in water, leaving behind a red powder, and the solution does not contain a trace of sodic ferrofulminate. On adding sodic hydrate, however, union of the components again takes place, and the solution contains sodic ferrofulminate, which can be obtained on allowing the solution to evaporate.

The red dissociated salt just mentioned possesses very explosive properties. It is just as dangerous as sodic fulminate,* and on this account it was never possible to carry out a complete analysis of the salt; even when mixed very carefully with oxide of copper, on heating invariably a violent explosion took place.† The quantitative

* Journ. f. prakt. Chem., [2.], XXXII. 231.

† The explosion is so sudden that not a gas bubble appears in the potash bulb (5 times noticed), and the combustion tube is shattered completely only where the substance was present.

determination of the iron and sodium offered at first some difficulty, because, on decomposing the salt with hydrochloric and nitric acids, always a small amount of substance crystallizing in green leaflets is formed, which is insoluble in aqua regia. The salt was finally decomposed by treating first with a small amount of dilute sulphuric acid, and then evaporating to dryness and igniting. The residue was then dissolved in hydrochloric acid, with addition of a small amount of nitric acid, and the iron and sodium determined in the usual way.

4.754 grams yellow salt, dried between filter paper, lost on standing over H_2SO_4 in a vacuum, after two days, 1.5806 grams H_2O ; after four days, 1.8167 grams H_2O ; after six days, 1.8996 grams H_2O ; on further standing, no further loss of weight was noticed.

	Theory for $\text{Na}_4\text{Fe}(\text{ONC})_6 \cdot 2\text{H}_2\text{O} + 16\text{H}_2\text{O}$.	Found.
16 H_2O	39.80	39.96

The red powder remaining is very hygroscopic, and still contains two molecules of crystal water.

1.0073 grams substance gave 0.1760 gram Fe_2O_3 .

0.8154 gram substance gave 0.5380 gram Na_2SO_4 .

0.6999 gram substance gave 0.1282 gram Fe_2O_3 and 0.4609 gram Na_2SO_4 .

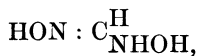
	Theory for $\text{Na}_4\text{Fe}(\text{ONC})_6 \cdot 2\text{H}_2\text{O}$	Found.
Na	21.10	21.36
Fe	12.84	12.12
		21.33
		12.73

An attempt was made to obtain, by oxidation of this salt with bromine and water, a fulminic acid double salt corresponding to sodic ferricyanide, but without success.

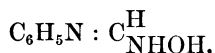
V. ON FULMINIC ACID AND ITS ESTERS. — THE CARBYLOXIM-ESTERS, $\text{C} : \text{NOR}$.

The experiments described above make it clear that it is not possible to obtain free fulminic acid from its salts by treatment with acids, because the acids always react first on the tremendously reactive bivalent carbon atom present in these salts; and for this reason oximes of formic acid derivatives are invariably obtained, which, although they can readily be converted back again into fulminic acid salts, never yield, when they decompose, the free fulminic acid. In this connection an experiment carried out with isuretine is of interest. On heating alcoholic solutions of isuretine and hydroxylamine hydrochloride (in molecular quantities) an interaction with formation of ammonium

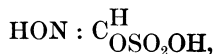
chloride and of oxyisuretine very quickly takes place. On attempting to distil off the alcohol, white fumes are noticed, which decompose with some violence and the solution has an odor resembling very closely that of prussic acid. On evaporating the solution over sulphuric acid in a vacuum, a yellow coloration is noticed (after most of the alcohol has disappeared), and after a short time the residue decomposes spontaneously with a hissing noise and tremendous evolution of heat. It follows from this experiment that oxyisuretine,



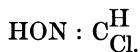
is a very unstable substance, and decomposes probably at first into carbyloxime, $\text{C} : \text{NOH}$, and into hydroxylamine. This decomposition is entirely analogous to that of phenylisuretine,



and also especially to that of formylsulphate-oxime,



and of formylchloridoxime,



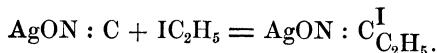
The sum total of the results presented in this paper lead to the conclusion that the free fulminic acid is a very unstable compound, which possesses a smell that cannot be distinguished from that of prussic acid. It follows further, however, that a series of ethers of this acid must exist of the general formula $\text{C} : \text{NOR}$, which must in their properties and their odor show the greatest resemblance to the esters of prussic acid, the alkylisocyanides, $\text{RN} : \text{C}$. Although I have not yet succeeded in isolating and analyzing a carbyloximether, $\text{C} : \text{NOR}$, the following observations are sufficient to make it extremely probable that such esters do exist.

The Action of Ethyliodide on Silver Fulminate.—Calmels * states, that on treating silver fulminate with ethyliodide, α and β nitropropylene and ethylisocyanide are formed. I have repeated his experiments, and observed that, on heating silver fulminate with ethyliodide and absolute ether to 50° , or on allowing these substances to stand at

* Comptes Rendus, XCIX. 794.

ordinary temperature, after a time most tremendous explosions take place; these can be entirely avoided as follows. 28.7 grams silver fulminate, 50 grams ethyliodide, and 38 grams absolute ether are brought into a flask, which is constantly kept in cold water, and allowed to stand thus for three weeks, taking care to shake well from time to time. At first, in the course of the reaction, a very strong smell of ethylcyanate is noticed (Calmels says smell of chlorpicrin) and towards the end a smell resembling that of ethylisocyanide is noticed.

The investigation of the products formed has shown that they *consist chiefly of ethylcyanate and its polymer ethylcyanurate*, whereas very little of the substance smelling like ethylisocyanide is formed. It seems to me, however, extremely probable that this product is not ethylisocyanide, but ethylcarbyloxim, $C : NOC_2H_5$, the formation of which from silver fulminate, $C : NOAg$, and ethyliodide is self-evident. The formation of ethylcyanate, or of its polymer, which is the chief product of the above reaction, is easily explained by an addition of ethyliodide to the unsaturated carbon atom present in silver fulminate,



The addition product is then converted by Beckmann's rearrangement into ethylcyanate and silver iodide.



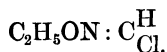
26 grams isuretine were heated, in alcoholic solution, with one molecule of sodium ethylate and ethyliodide ($1\frac{1}{4}$ molecules), for three hours with reversed condenser; the alcohol was thereupon distilled off, and a strong smell of isonitrile and ammonia was noticed. The residue was dissolved in water and repeatedly extracted with ether. After distilling off the ether, and fractionating the liquid remaining, 3 grams of an ethereal weak basic smelling oil were obtained, which boils without decomposition at 170° – 175° . Up to the present only 7 grams of this oil have been obtained, which, in view of an analysis of a platinum double salt obtained from it, must be regarded as ethoxyformamidine. It is easily soluble in water; a portion was dissolved in hydrochloric acid, and the evaporated solution taken up in alcohol and treated with platinic chloride. On addition of ether a yellow oil separates out, which, on rubbing with a glass rod, solidifies. The salt was recrystallized from alcohol and ether, and obtained in yellow quadratic plates, melting at 153° .

0.3055 gram substance dried at 100° gave 0.1013 gram Pt.

0.3018 gram substance dried at 100° gave 26.6 c.cm. N₂ at 17° and 749 mm.

	Theory for (C ₃ H ₅ N ₂ O, HCl) ₂ PtCl ₄ .	Found.
Pt	33.16	33.16
N	9.57	10.07

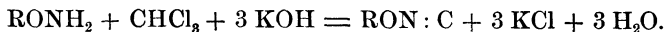
The remaining ethoxyformamidine was dissolved in 4 molecules dilute hydrochloric acid and treated, in the cold, with 1 molecule of sodic nitrite.* A copious evolution of nitrogen is noticed, and after standing for thirty minutes the solution is extracted with ether, and the ethereal solution washed with dilute sodic hydrate and then dried with calcic chloride. An oil is obtained which contains much chlorine, and seems to boil without decomposition, and at higher temperatures possesses a very sharp odor. It is very probable that it consists of ethoximformylchloride,



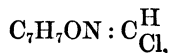
On heating the oil, which is soluble in water, with concentrated caustic alkalis, a strong smell of isonitrile is observed, which can only be due to the formation of ethylcarbyloxime. Ethoximformylchloride seems, however, in comparison with formylchloridoxime, to be remarkably stable, and is split, on treatment with alkalis, chiefly into formic acid, ethoxylamine, and potassic chloride.

The Action of Chloroform and Alcoholic Potash on α Benzylhydroxylamine.

The esters of carbyloxime ought, however, to be obtained most easily from α alkylated hydroxylamines by means of Hofmann's reaction,



On adding a mixture of α benzylhydroxamine † (10.4 grams) and chloroform (17.3 grams) to a solution of 19.2 grams potassic hydrate in 70 grams alcohol, an energetic reaction takes place, and a strong smell of isocyanide is noticed. Benzylcarbyloxime, C₇H₇ON : C, has, however, been formed only in minute quantities, and 7 grams unchanged α benzylhydroxylamine were recovered. The reason for this seems to me to be due to the fact that the intermediate product,



* Tiemann and Krüger, Ber. d. chem. Ges., XVIII. 1732.

† Behrend and Leuchs, Ann. Chem. (Liebig) 257, 205.

which must be formed in the reaction,* is very stable, just as is the case with ethoximformylchloride mentioned above, and therefore it is split chiefly into α benzylhydroxylamine, formic acid, and potassic chloride.

In the above work on bivalent carbon, which will be continued in various directions, I have been assisted with great skill and with remarkable perseverance by Dr. M. Ikuta, to whom I wish also here to express my warmest thanks.

* Ann. Chem. (Liebig), CCLXX. 308.